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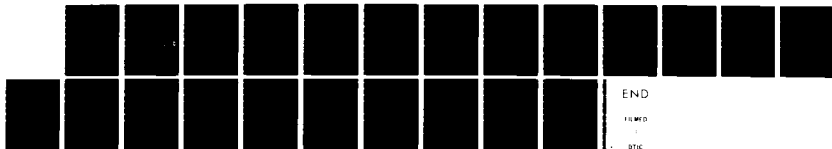
CHEMICALLY DERIVATIZED SEMICONDUCTOR PHOTOELECTRODES  
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CHEMISTRY M S WRIGHTON 01 JUN 83 TR-37-ONR

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Semiconductor-based photoelectrochemical cells are the best man-contrived devices for the direct conversion of sunlight to electrical or chemical energy using chemically-based systems. Deliberate modification of the surface of the semiconductor photoelectrode is useful in improving the rate of desired processes and in suppressing undesirable anodic corrosion associated with photoanodes. Illustrations of the use of surface modification will be presented with specific examples coming from work with molecular-based derivatizing reagents and from the use of metals or metal oxides coated onto the photoelectrode surface.

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TECHNICAL REPORT NO. 37

"CHEMICALLY DERIVATIZED SEMICONDUCTOR PHOTOELECTRODES"

by

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Prepared for publication in the Journal of Chemical Education

June 1, 1983

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# CHEMICALLY DERIVATIZED SEMICONDUCTOR PHOTOELECTRODES

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## Abstract:

Semiconductor-based photoelectrochemical cells are the best man-contrived devices for the direct conversion of sunlight to electrical or chemical energy using chemically-based systems. Deliberate modification of the surface of the semiconductor photoelectrode is useful in improving the rate of desired processes and in suppressing undesirable anodic corrosion associated with photoanodes. Illustrations of the use of surface modification will be presented with specific examples coming from work with molecular-based derivatizing reagents and from the use of metals or metal oxides coated onto the photoelectrode surface.

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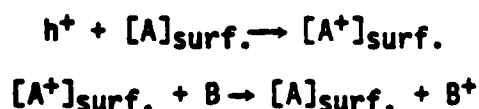
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Semiconductor-based photoelectrochemical cells are now known to be capable of effecting the sustained conversion of solar energy to electricity or to chemical fuel in the form of redox products.<sup>1-3</sup> Not surprisingly, it has been concluded that the properties of the surface of the semiconductor photoelectrode in contact with the electrolyte solution govern the performance of these energy conversion devices. The key characteristics of photoelectrode durability, output photovoltage, and output photocurrent can be favorably altered by modification of the surface of the semiconductor photoelectrode.<sup>4</sup> The aim of this article is to highlight the significant results from modification of photoelectrode surfaces.

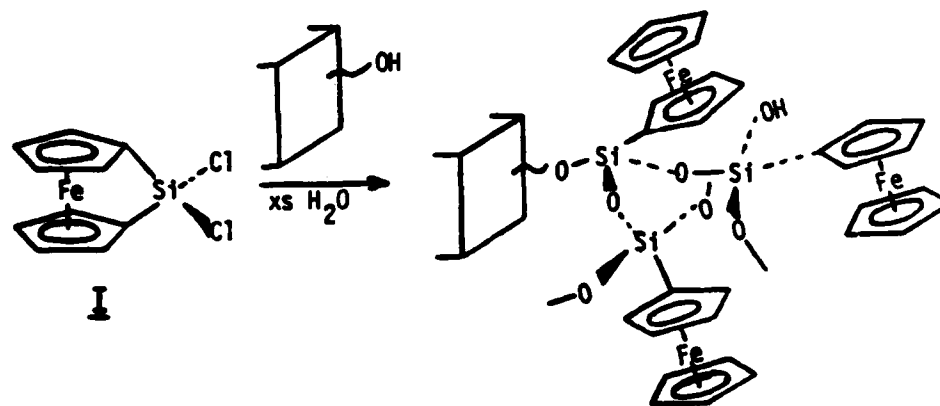
Suppression of Photocorrosion of n-Type Semiconductors. It is well-known that an n-type semiconductor can undergo decomposition when used as a photoanode in an electrochemical cell.<sup>5-7</sup> Clearly, if an n-type semiconductor is to be used for the sustained conversion of light to chemical or electrical energy in a photoelectrochemical cell, the photoanodic decomposition of the electrode must be suppressed. It is also known that there are desirable interfacial redox reactions that can successfully compete with the photoanodic decomposition of the electrode.<sup>1</sup> For example, the oxidation of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  can compete with the photooxidation of n-type Si in non-aqueous solutions.<sup>8</sup> The point is that while all n-type semiconductors are thermodynamically unstable when illuminated with  $>$  band gap light, reductants can kinetically compete for the photogenerated oxidizing equivalents (holes,  $h^+$ ) that are available at the surface of the semiconductor. Thus, the ability to sustain a desired photoanodic process can be viewed as a kinetic competition between two thermodynamically favorable processes. Thermodynamics defines the realm of possibility, but kinetics can fortunately be manipulated to realize a desired objective.

When a reductant A is found to suppress the photoanodic corrosion of an n-type semiconductor electrode it may or may not be easy to find other reagents that will also be successful in competing for the photogenerated  $h^+$ . It is sometimes the case that the desired reaction is  $B \rightarrow B^+$ . This may be a process that does not effectively compete with the photoanode decomposition, owing to poor kinetics for the  $h^+ + B \rightarrow B^+$  process compared to the decomposition involving the photogenerated  $h^+$ . In such a case it may be possible to modify the surface of the semiconductor with a derivative of A in order to suppress the corrosion of the photoelectrode while preserving the ability to oxidize B:



The role of the surface-confined A,  $[A]_{\text{surf.}}$ , is to capture the photogenerated oxidizing equivalent to preclude the anodic corrosion of the semiconductor, forming  $[A^+]_{\text{surf.}}$ . The solution species B can be oxidized to  $B^+$  by  $[A^+]_{\text{surf.}}$  in a heterogeneous reaction regenerating  $[A]_{\text{surf.}}$  in the process. Thus, whether the oxidation of B can be effected depends on the oxidizing power of  $[A^+]_{\text{surf.}}$  and the kinetics for its reaction with B. In many instances the redox properties of the surface-confined redox system and its solution analogue are very similar.<sup>9</sup> It can be concluded, therefore, that an n-type semiconductor functionalized with the  $[A^+/A]_{\text{surf.}}$  system should be capable of effecting the sustained photooxidation of B if the  $A^+/A$  system in solution is capable of both suppressing the photodecomposition of the anode and oxidizing B. The main advantage is that the modified n-type semiconductor should be useful in effecting many desirable redox processes, not just the oxidation of A.

The functionalization of semiconductor surfaces can be brought about in many ways.<sup>4</sup> Consider the example cited above of n-type Si made durable by the addition of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  to a non-aqueous solution.<sup>8</sup> A derivative of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ , I, is a reagent that can react with surface-OH groups and trace amounts of  $\text{H}_2\text{O}$  to yield more than monolayer quantities of the ferrocene-based redox material covalently anchored to a surface:



It has been demonstrated that n-type Si electrodes derivatized in this way can be used to sustain the photooxidation of B for any B oxidizable with the solution species  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2^+$ , the oxidized form of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ .<sup>10,11</sup> In this system the  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  is the reductant A of the foregoing paragraph. The additional finding is that the surface-confined material derived from I also allows the use of n-type Si photoanodes in aqueous electrolytes where the photoanodic formation of  $\text{SiO}_x$  is most severe and where the  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  itself is not useful owing to its insolubility. The surface-confined reagent, however, is useful and allows the use of n-type Si photoanodes for many other reactions other than the oxidation of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  in non-aqueous solvents.

Unfortunately, the surface-confined material derived from I is not useful in effecting the oxidation of  $\text{H}_2\text{O}$  at an n-type Si photoanode. The oxidizing power of the  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2^+$  is not sufficient to oxidize  $\text{H}_2\text{O}$ . Further, it is unlikely that simple one-electron redox reagents would have good kinetics for

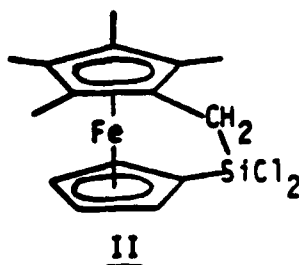


the four-electron oxidation of  $\text{H}_2\text{O}$  to form  $\text{O}_2$ . Another approach to electrode modification has yielded some success in this regard, however. The surface of n-type Si can be modified by the deposition of Pt followed by a heat treatment to yield a platinum silicide surface. Electrodes treated in this way can be durable with respect to anodic corrosion in aqueous electrolyte solutions for the oxidation of halides to form halogens.<sup>12</sup> Further modification with  $\text{RuO}_x$  yields a surface from which evolution of  $\text{O}_2$  from  $\text{H}_2\text{O}$  oxidation can be detected upon excitation with light absorbed by the n-type Si. The platinum silicide protective coating differs from the coating derived from reagent I in that it has electronic conductivity whereas  $\text{h}^+$  movement through the film from I can only occur through a sequence of electron transfer processes involving the individual ferrocene-based redox centers. A faster movement of  $\text{h}^+$  through the metallic overcoat can be expected, but the surface derived from treatment with reagent I has molecular properties that may allow unique chemical reactions to be effected. The fast  $\text{h}^+$  movement and a surface having exposed molecular species can both be realized by functionalizing the photoanode surface with polypyrrole, an electronically conducting polymer formed by the anodic polymerization of pyrrole.<sup>13-16</sup>

Improvement of Rate of a Desired Anodic Process. In many cases an n-type semiconductor can be made more durable by surface modification. However, it is not always true that the modification used to bring about durability allows the redox event of interest to be observed with high efficiency. When electrode decomposition is not occurring and the desired redox event is not fast, recombination of the photoexcited electron and the photogenerated hole can occur. This means that the optical excitation is degraded into heat or emitted as lower energy optical radiation. When there is a thermodynamically possible process that occurs slowly catalysts may be useful in improving the

rate. One example has already been mentioned, namely the case of n-type Si made durable by the platinum silicide but which does not yield efficient oxidation of  $H_2O$ . The rate of oxidizing  $H_2O$  can be improved by the deposition of the  $RuO_x$ , known to be a good surface from which to evolve  $O_2$ .<sup>12</sup> More recently, the efficiency for  $Cl_2$  generation from the photooxidation of  $Cl^-$  at illuminated n-type  $MS_2$  ( $M = Mo, W$ ) has been significantly improved by the deposition of a catalytic amount of Pt onto the  $MS_2$  electrode surface.<sup>17</sup>

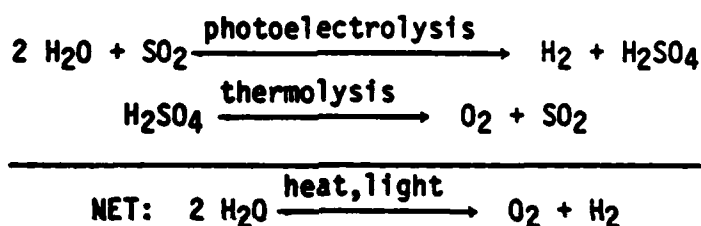
The examples of rate improvement cited in the paragraph above do not involve the use of molecules as the catalytically active species. Rather, the catalyst is one which can be useful in bringing about oxidations that involve more than one oxidizing equivalent per product molecule. In some cases the catalysis may be best brought about using a molecular entity. One such example involves the oxidation of large biological molecules such as horseheart cytochrome c, cyt c, that do not rapidly exchange electrons with electrodes for a variety of reasons. However, small redox molecules do readily exchange electrons with large biological molecules and are used as redox "mediators".<sup>18</sup> Thus, surface-confined mediators should be useful in improving the rate of photooxidation at illuminated n-type semiconductor electrodes. Recent studies of n-type Si derivatized with reagent II establish that photooxidation of the



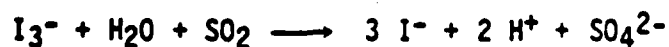
reduced form of cyt c can be effected at the modified surface.<sup>19</sup> The reaction is not doable at the "naked" photoanode because the kinetics are poor and the decomposition of the photoanode is severe. Improving the durability of the

n-type Si by using a procedure such as the platinum silicide is not likely to be successful, since the problems that plague biological redox molecules will emerge at the platinum silicide surface exposed to the electrolyte solution. The ability to effect the efficient photooxidation of biological substances may ultimately be useful in oxidizing H<sub>2</sub>O, since O<sub>2</sub> evolution from H<sub>2</sub>O oxidation occurs in the natural photosynthetic system.

Catalysis of the oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> in strong acid solution<sup>20</sup> provides a final example of surface modification of interest in connection with semiconductor photoanodes. Interest in this system stems from the prospect that a hybrid scheme for water splitting can be envisioned:



The photooxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> can be effected in strong acid solution at illuminated n-type MS<sub>2</sub> electrodes. The key is that the solution must contain a small amount of the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple. The I<sub>3</sub><sup>-</sup>/I<sup>-</sup> system specifically adsorbs onto the MS<sub>2</sub> to bring about a favorable set of interface energetics. The adsorption of the I<sub>3</sub><sup>-</sup>/I<sup>-</sup>, though, is not irreversible as in the covalent attachment of reagents I and II. Rather, the adsorption of the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> is rapidly reversible. Nonetheless the interaction of the MS<sub>2</sub> with the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> couple is sufficiently strong to bring about a favorable change in the interface energetics for the SO<sub>2</sub> oxidation. Further, the primary photo-oxidation product, I<sub>3</sub><sup>-</sup>, from the oxidation of I<sup>-</sup> can rapidly oxidize the SO<sub>2</sub>:

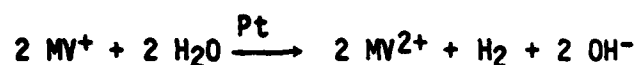


Thus, in the photoelectrolysis of  $\text{H}_2\text{O}/\text{SO}_2$  in acid solution the  $\text{I}_3^-/\text{I}^-$  plays two roles: the strong interaction with the  $\text{MS}_2$  surface brings about a change in interface energetics that improves the output photovoltage and the redox chemistry of the adsorbed  $\text{I}_3^-/\text{I}^-$  system brings about an improvement in the rate of the  $\text{SO}_2$  oxidation. The n-type  $\text{WS}_2$  based cell for the photoelectrolysis of  $\text{H}_2\text{O}/\text{SO}_2$  represents one of the most efficient energy conversion devices for the direct generation of energy-rich materials where visible light is the only energy input.<sup>20</sup> Further, the surface modification in situ by the  $\text{I}_3^-/\text{I}^-$  redox couple exploits the surface chemistry of the  $\text{MS}_2$ ; the favorable change in interface energetics by adsorption of the mediator system is not common occurrence.

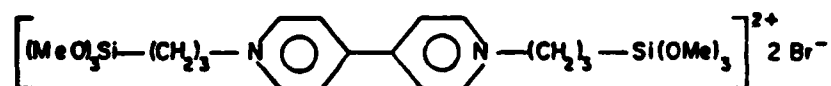
Improvement of Rate of a Desired Cathodic Process. Photocathodic processes can be efficiently effected at p-type semiconductors where the photoexcited electron,  $\text{e}^-$ , not the oxidizing  $\text{h}^+$ , comes to the surface of the electrode available for some redox event. The problem of anodic decomposition of p-type semiconductors is often nonexistent, perhaps because the reducing equivalents at the surface protect the surface from oxidative decomposition. Generally, the redox process that has been the object of most attention, namely  $\text{H}_2$  formation, does not occur with good kinetics at many electrodes.<sup>21</sup> Semiconductors are unexceptional in that they do not have good kinetics for  $\text{H}_2$  evolution.<sup>22</sup> Thus, catalysis of  $\text{H}_2$  evolution is desirable. Surface modification has proven to be useful in significantly improving the efficiency for the photocathodic evolution of  $\text{H}_2$  from  $\text{H}_2\text{O}$  via catalysis of the reduction process.

One approach to catalyzing the evolution of  $\text{H}_2$  emerged from the demonstration that kinetics, not energetics, for the process are the limiting factor.<sup>22</sup> The result that demonstrates that the kinetics are limiting comes from the comparison of the efficiency for reducing N,N'-dimethyl-4,4'-bipyri-

dinium,  $MV^{2+}$ , versus  $H_2O$  at a pH where  $MV^{2+}$  and  $H_2O$  are equally difficult to reduce in thermodynamic terms. Nearly zero efficiency is obtained for the reduction of  $H_2O$ , whereas good efficiency can be obtained for the reduction of  $MV^{2+}$  at illuminated p-type semiconductors such as Si, InP, and GaAs.<sup>22</sup> The reduction of  $MV^{2+}$  to form  $MV^+$  is known to occur with good kinetics at many electrode surfaces and again the semiconductors are unexceptional. The important conclusion is that a reducing reagent,  $MV^+$ , that is just as potent a reductant as  $H_2$  can be produced at an illuminated p-type semiconductor with good efficiency. Further, it is known that the  $MV^{2+}/^+$  system can be equilibrated with the  $H_2O/H_2$  via Pt catalysis:



Thus, derivatization of p-type Si electrode surfaces with the N,N'-dialkyl-4,4'-bipyridinium reagent, III, followed by deposition of a noble



### III

metal such as Pt or Pd results in an efficient photocathode.<sup>23</sup> Like reagents I and II, reagent III has hydrolytically unstable functionality that allows it to react with surface-OH groups and with  $H_2O$  to bring about the attachment of greater than monolayer quantities of the redox centers. The 2+ charge on the monomer units can be useful in incorporating the Pt or Pd precursor inasmuch as metal complex anions such as  $PtCl_4^{2-}$  can be electrostatically bound and subsequently reduced to the active zero valent Pt. The incorporation of the Pt or Pd is essential to efficient  $H_2$  generation, since the reduced form of

the surface-confined material from III does not have good kinetics for reaction with  $H_2O$  to produce  $H_2$ . The Pt or Pd equilibrates rapidly with both the surface-confined redox material and with the  $H_2O/H_2$ . Long term durability of surface-confined catalysts remains an important concern, but the success realized so far is encouraging.

It is also possible to significantly improve the kinetics for the photo-reduction of  $H_2O$  by the deposition of Pt onto the surface of the semiconductor in a manner similar to that in improving the efficiency for  $Cl_2$  formation at the illuminated n-type  $MS_2$ .<sup>24</sup> However, direct deposition of Pt onto p-type semiconductors has the tendency to form an ohmic contact with the semiconductor that can completely remove the photovoltage.<sup>25</sup> The use of the redox polymer can prevent the semiconductor surface from being contacted by the Pt, precluding reduction in the output photovoltage. In principle, any mechanism to bring about the catalysis that does not alter overall energetics (as happens in the  $I_3^-/I^-$  case described above) will give the same theoretical efficiency. Whatever the procedure, it is clear that modification of the surface of a photocathode can significantly improve the efficiency for production of  $H_2$ .

The molecular properties of the surface-confined material derived from III can also be exploited. The photoreduction of the oxidized form of cyt c can be effected at a p-type Si electrode functionalized with III, whereas the reduction cannot be detected at the naked electrode even though it is durable in aqueous solution.<sup>25</sup> Interestingly, the  $MV^{2+}/+$  system is a good mediator for biological redox reagents that are known to be able to catalyze the reduction of  $H_2O$  to produce  $H_2$ , the reduction of  $N_2$  giving  $NH_3$ , and the reduction of  $CO_2$  to produce  $HCOOH$ . None of these processes has good kinetics at the naked p-type semiconductor photocathodes, and yet all of these would be

significant targets for practical solar conversion systems.

### CONCLUSIONS

The deliberate modification of semiconductor photoelectrodes to improve durability and to enhance the rate of desirable interfacial redox processes has been summarized for a variety of systems. Modification with molecular-based systems or with metals or metal oxides has yielded results that signal an important role for surface modification in devices for fundamental study and in practical energy conversion. A question that arises is: Are there any direct solar fuel producing systems that will not require modification and redox catalysis at interfaces?

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